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Infrared Absorption Spectra of Some Epoxy Compounds

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In speculating on the mechanisms of the autoxidation of unsaturated compounds, some investigators have postulated that various kinds of heterocyclic oxygen ring compounds are formed. There is no reliable evidence, however, of the formation of any type of oxygen ring compounds except oxirane compounds. Infrared absorption spectra of a series of pure epoxy compounds from 2 to 15 microns have been obtained and interpreted. Oxirane derivatives of terminally monounsaturated compounds show two characteristic absorption bands near 11 and 12 microns; oxirane derivatives of *cis* monounsaturated fatty acids, esters, and alcohols show a characteristic band at 11.8 to 12 microns, whereas those from the *trans* isomers show a band at 11.2 to 11.4 microns; absorption bands characteristic of 5- and 6-membered carbon-oxygen rings have been noted. The spectra of the long-chain epoxy acids and alcohols are dependent on physical state. The spectra are primarily intended to serve as reference data in the application of infrared spectrophotometric methods to the analyses of autoxidation mixtures.

IN SPECULATING on the mechanism of the reaction of unsaturated compounds with oxygen, some investigators have postulated that various kinds of heterocyclic oxygen ring compounds are formed. There is no reliable evidence of any type of heterocyclic oxygen ring compound except oxirane compounds, which have been isolated from such reactions. Even when oxirane compounds are not isolated, they can be determined quantitatively in systems involving oxidation of monounsaturated compounds (11). In the oxidation of polyunsaturated compounds, however, conjugated materials, which form early in the reaction, interfere with the analytical determination of oxirane compounds. The authors know of no specific analytical method for detection or quantitative determination of other types of ring oxygen, especially when present in small quantities and with other functional groups.

For the qualitative (3), as well as the quantitative or semi-quantitative (1), determination of functional groups, infrared spectroscopy has recently become a useful tool. Little has been reported, however, on the spectra of heterocyclic oxygen com-

pounds. The few published spectra (2) cover only a limited range, and the purity of the compounds is unknown.

Since this paper was submitted, Field, Cole, and Woodford (4) reported infrared absorption data on eight oxirane compounds. They concluded that only the 1250 cm^{-1} (8μ) band could be identified with reasonable certainty as characteristic of the oxirane group.

Before infrared spectroscopy can be used to detect the presence or absence of heterocyclic oxygen ring compounds in oxidation reaction mixtures, and in other applications, it is essential to have reference spectra of pure compounds. This paper, which reports an extension of earlier work (7), gives the infrared absorption spectra from 2 to 15 microns of thirteen pure oxirane compounds, tetrahydropyran, tetrahydrofuran, and dioxane. The spectra are interpreted in the discussion.

EXPERIMENTAL

Spectrophotometer. The spectrophotometer and techniques used were identical with those described in a previous paper

Table I. Characteristics of Reference Compounds

Reference Compound	B.P.		M.P. ° C.	n_D	Oxirane Oxygen, % (11)	Method of Preparation and/or Literature Reference (9)
	° C.	Mm.				
Glycidol	39.3	2.5	...	1.4293 (25°)	21.3	Distillation of best commercial grade through efficient column (50 to 120 plates)
Propylene oxide	33.5	1.3670 (20°)	...	
3,4-Epoxy-1-butene	66	1.4176 (20°)	...	
1,4-Dioxane	101	1.4223 (20°)	...	
Tetrahydrofuran	66	1.4074 (20°)	...	
Tetrahydropyran	88	1.4210 (20°)	...	
1-Phenyl-1,2-epoxyethane (styrene oxide)	100	40	...	1.5295 (30°)	...	(10)
1,2-Epoxydecane	87.6	10	...	1.4249 (30°)	9.81	
1,2-Epoxydodecane	98-99	3.5	...	1.4314 (30°)	8.45	
1,2-Epoxytetradecane	101.5-102.4	0.5	...	1.4363 (30°)	7.23	
<i>cis</i> -9,10-Epoxyoctadecanoic acid	59.8	...	5.38	(5)
<i>trans</i> -9,10-Epoxyoctadecanoic acid	55.6	...	5.37	(5)
Methyl <i>cis</i> -9,10-epoxystearate	120-128	0.015	...	1.4479 (30°)	5.10	(5)
Methyl <i>trans</i> -9,10-epoxystearate	126-128	0.018	...	1.4449 (30°)	5.02	(5)
<i>cis</i> -9,10-Epoxyoctadecanol	53	...	5.60	(5)
<i>trans</i> -9,10-Epoxyoctadecanol	48.3-48.7	...	5.64	(5)
<i>n</i> -Decane	Natl. Bur. of Standards sample
Thermally treated <i>cis</i> -9,10-epoxystearic acid	<i>cis</i> -9,10-Epoxyoctadecanoic acid, m.p. 59.8°, heated 26 hours at 100° (8)

(7). The spectra of the liquids were determined in a 0.033-mm. liquid cell, except the spectrum of glycidol, which was determined in a 0.015-mm. cell. The spectra of the solid compounds were determined on 10% solutions in carbon bisulfide in a 0.115-mm. cell and also on the solid as Nujol mulls.

Materials Used. The reference compounds employed, some of their characteristics, and methods of preparation are shown in Table I.

RESULTS AND DISCUSSION

Figures 1 to 6 show spectra for the various compounds as plots of per cent transmission against wave length in microns on a linear wave-length scale. Wave-length positions of absorption maxima, read from the original records, are shown on each curve.

Oxirane Derivatives of Long-Chain Olefins. To determine the effect of introducing the oxirane ring into a long-chain compound, spectra of the oxirane derivatives of three terminally unsaturated long-chain olefins (1-decene, 1-dodecene, and 1-tetradecene) were obtained. In Figure 1 these spectra are compared with that of a standard National Bureau of Standards sample of *n*-decane at the same cell thickness. Bands of medium intensity near 7.0, 7.9, and 8.8, as well as two strong bands near 10.9 and 11.9 microns, are present in the spectra of the three oxirane derivatives but absent in that of the hydrocarbon. 1-Dodecene and 1-tetradecene, like the saturated hydrocarbon, do not absorb appreciably at these wave lengths at comparable sample thickness. Probably the first three of these bands are caused by various C—O vibration modes, and the two

strong bands near 10.9 and 11.9 microns are caused by motions of the oxirane ring, which vibrates as a unit.

Oxirane Compounds of Lower Molecular Weight. Figure 2 shows spectra of four additional compounds that contain the oxirane ring in the terminal position. The origin of many of the bands can be deduced from the molecular structure, in conjunction with well-known frequency assignments. All four compounds show strong bands in the vicinity of those observed near 11 and 12 microns in the long-chain oxirane compounds of Figure 1. Propylene oxide and glycidol show these bands altered in relative intensity but at nearly the same wave lengths

as do the compounds of Figure 1. In the spectrum of 3,4-epoxy-1-butene, however, the longer wave-length band of this pair has undergone a considerable shift, probably as a result of the effect of the adjacent double bond on the vibration involved. Ambiguity arises in the spectrum of 1-phenyl-1,2-epoxyethane (styrene monoxide) because of the possibility that strong bands in this region are caused by the monosubstituted aromatic ring. (Styrene, for example, has a strong band at 11 microns.)

Oxirane Derivatives of Long-Chain 9-Monounsaturated Acids, Esters, and Alcohols. From the foregoing discussion, it may be tentatively concluded that an oxirane ring in the terminal position in a molecule causes a pair of absorption bands near 11 and 12 microns. Figure 3 shows spectra of the oxirane derivatives of oleic acid, methyl oleate, and oleyl alcohol; also shown are

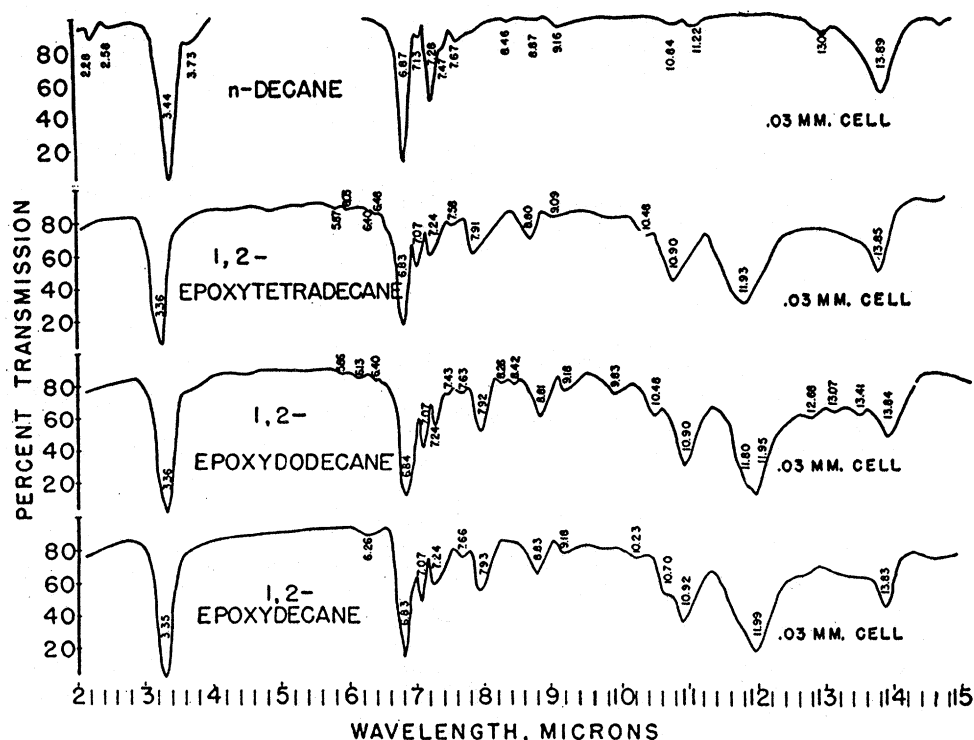


Figure 1. Infrared Spectra of *n*-Decane and Some Pure Oxirane Derivatives of Long-Chain 1-Olefins

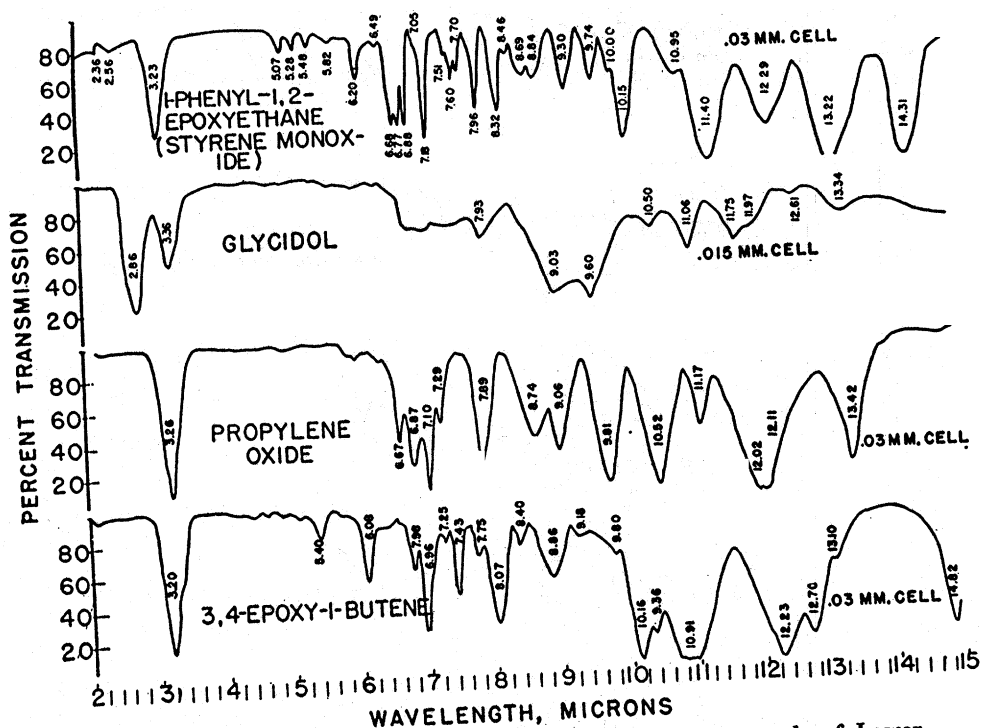


Figure 2. Infrared Spectra of Some Pure Oxirane Compounds of Lower Molecular Weight

the spectra of the oxirane derivatives of the *trans* isomers of these three compounds (elaidic acid, methyl elaidate, and elaidyl alcohol). The effect of introducing the oxirane group into these long-chain acids, esters, and alcohols is best illustrated by comparing (a) the spectrum of each epoxy acid with that of stearic acid, (b) the spectrum of each epoxy ester with that of methyl stearate, and (c) the spectrum of each epoxy alcohol with that of stearyl alcohol (*n*-octadecanol). The three spectra required for this comparison were discussed in a previous paper (6). Such a comparison shows that the spectra of the *cis*-epoxy acid, ester, and alcohol are qualitatively similar to those of stearic acid, methyl stearate, and *n*-octadecanol, respectively, except for a new band near 12 microns in each case. Similarly, the spectra of the *trans*-epoxy acid, ester, and alcohol show close qualitative similarity to those of stearic acid, methyl stearate, and *n*-octadecanol, respectively, except for a new band near 11.2 microns. The 11.2-micron band in each of the *trans* oxirane compounds is somewhat stronger relative to other bands in the spectrum than is the 12-micron band in the corresponding *cis* compound. By analogy with the changes caused by introducing the oxirane ring into the long-chain hydrocarbons, these changes in the 7-, 7.9-, and 8.8-micron region were expected. Because C—O linkages are already present in the comparison compounds, however, such changes are not readily apparent.

On the basis of these observations, together with those noted in connection with the spectra of Figures 1 and 2, the authors have tentatively concluded that the oxirane ring in oxirane compounds derived from long-chain internally monounsaturated compounds having the *cis* configuration at the double bond causes an absorption band near 12 microns. This ring in the corresponding *trans* compounds causes a band near 11.2 microns. If the oxirane compound is derived from a terminally unsaturated compound, bands appear near both these wave lengths.

Effect of Physical State on Spectra of Solid Long-Chain Oxirane Compounds. The spectra shown in Figure 3 for the solid oxirane compounds (the epoxy acids and alcohols) were determined on solutions of these compounds in carbon bisulfide. To determine their spectra in the solid state, these four compounds

were also used as finely divided powders dispersed in Nujol (Figure 4). Although some minor differences were expected, the marked changes observed were surprising.

Comparison of Spectra of Epoxy Acids in the Solid State and in Solution. In a previous paper (7) it was pointed out that the long-chain fatty acids show several common spectral features, with reference to both position and general pattern of absorption maxima. As implied in the comparison with stearic acid above, the spectra of solutions of the two epoxy acids (Figure 3) exhibit all these typical spectral features, and therefore show a general resemblance to the spectra of unmodified fatty acids. In the spectra of solids (Figure 4), however, several of these typical absorption patterns have undergone drastic alteration. The broad absorption which appears in the 8-

micron region in the spectra of long-chain acids (7) is normal in the spectra of the epoxy acids in solution (Figure 3), but is replaced in the spectra of the solids by a series of sharp, well-resolved bands. These are intense in the *cis*-epoxy acid but weak in the *trans*-epoxy acid. The broad band near 10.7 microns, typical of acids (7), is normal in the spectra of solutions; in the spectrum of the *cis*-epoxy acid in the solid state, the strong 10.9-micron band probably corresponds to this absorption. If so, a substantial shift in wave length, together with a sharpening and increase in intensity (relative to other bands) has occurred. In the *trans*-epoxy acid, the weak 11.1-micron band evidently corresponds to this absorption, indicating an even greater shift and a decrease rather than an increase in intensity. The 13.9-micron band, related to CH₂ rocking motions in the long-chain acids (7), is also normal in the solution spectra of the epoxy acids. In the spectra of solids, the absorption of Nujol near this wave length obscures the issue; it is apparent, however, that this band in the spectrum of the *cis*-epoxy compound is either shifted to a shorter wave length or has been resolved into a doublet, probably the latter. In the spectrum of the *trans*-epoxy acid, this absorption appears as a single band in the spectra of both solution and solid. The weak band near 3.7 microns, believed to be a branch of the O—H . . . O "association" band in the spectra of fatty acids (7), appears to be normal in the spectra of solutions but is absent in the spectrum of the solid *trans*-epoxy acid and nearly absent in that of the *cis*-epoxy acid.

In addition to the alterations in the various absorption maxima which are typical of long-chain fatty acids, the 12-micron band attributed to the oxirane ring in the spectrum of the solution of the *cis*-epoxy acid has shifted to 11.8 microns in the spectrum of the solid and is greatly increased in sharpness and intensity. A similar increase, together with a shift from 11.2 to about 11.4 microns, has occurred in the oxirane ring band in the spectrum of the *trans*-epoxy acid. In general, the transition from solution to solid seems to be more marked for the *cis*- than for the *trans*-epoxy acid.

Comparison of Spectra of Epoxy Alcohols in the Solid State and in Solution. Although the spectra of solution of the two epoxy alcohols (Figure 3) show all the features common to long-

chain alcohols, the following changes are apparent in spectra of the solids (Figure 4): As expected, the hydroxyl stretching band near 2.8 microns in the spectra of solutions shifts to about 3.0 microns as a result of increased hydrogen bonding; the hydroxyl bending absorption near 9.5 microns, common to long-chain alcohols, shifts to about 9.3 microns; and the CH_2 rocking absorption at 13.9 microns, as in the spectrum of the *cis*-epoxy acid, is apparently resolved into a doublet.

In addition to these changes in the typical long-chain alcohol absorption bands, a number of new bands, entirely absent in spectra of the solutions, appear throughout spectra of the solids beyond about 8 microns as in the epoxy acids. The *cis* oxirane ring band has shifted from 12 to about 11.8 microns, the *trans* oxirane band has shifted from 11.2 to about 11.4 microns, and both bands are sharper and more intense.

Although some of the marked effects of physical state on the spectra of the solid epoxy compounds can be attributed to formation or breaking of hydrogen bonds or to dipolar association, many of the differences cannot be explained on this basis. A similar phenomenon has been observed by Richards and Thompson (6) in spectra of nonpolar hydrocarbons, compared in the solid and molten state. These workers found that the effect was more pronounced with long-chain paraffins than with "more rigid structures" such as the alkyl-substituted benzenes. As in the present case, many broad bands in the spectra of liquids split into two or more bands in the spectra of solids and, in general, bands in the spectra of solids were more numerous and sharper. As suggested by Richards and Thompson, passage from the liquid (or solution) to the solid state may involve changes in the potential energy functions associated with molecular vibration, and alteration in molecular symmetry and ordered arrangement may result in changes in the selection rules and principles governing the infrared activity of vibrations.

As noted above, the absorption band attributed to a vibration of the oxirane ring appears broad and weak in the spectra of solutions but sharp and strong in those of solids. This change may be related, at least in part, to the fact that in the ordered crystal state all individual groups of a given type probably vibrate in nearly identical field environments, and therefore absorb at nearly identical frequencies. The total absorption for all such groups would be concentrated over a narrow frequency range, producing a strong sharp band. In the unordered solution (or molten) state, however, variations in the environment of the individual groups would cause variations in exact positions of absorption

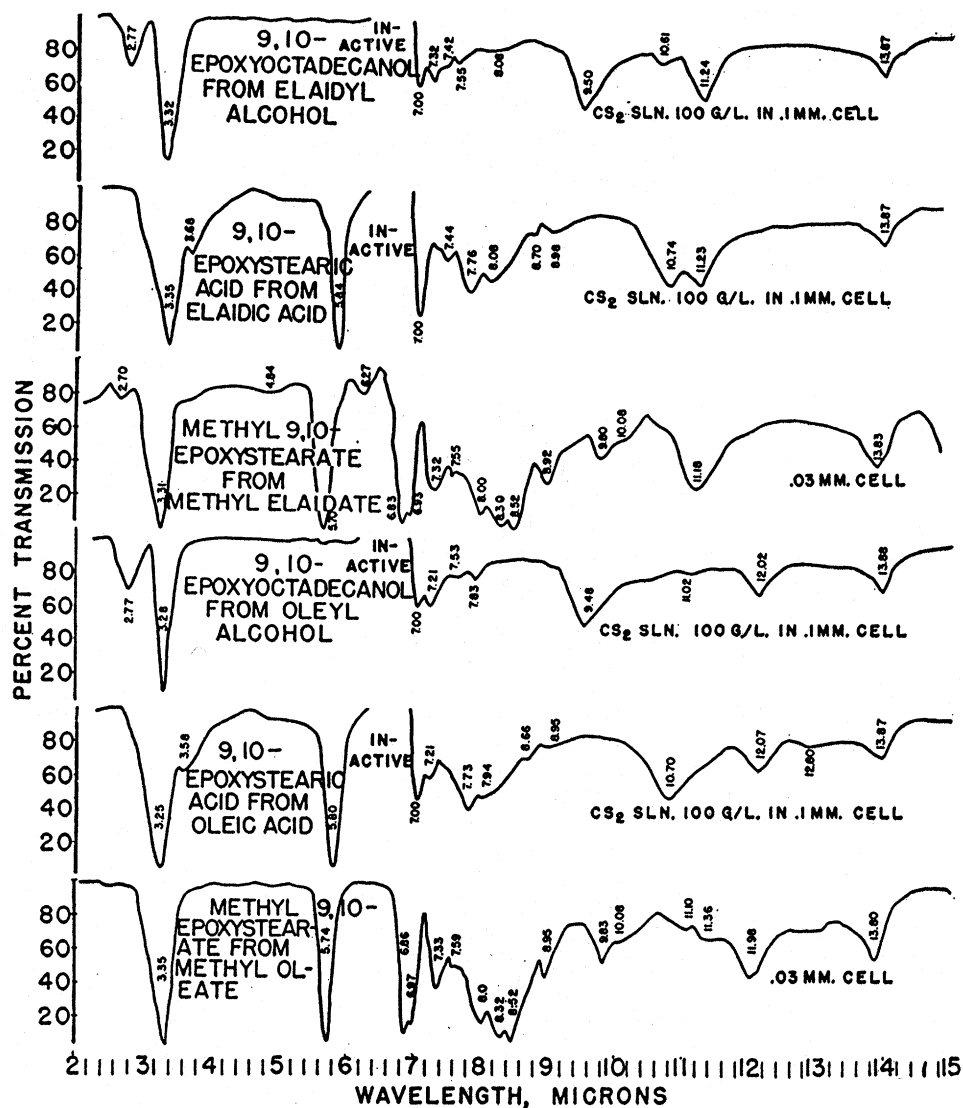


Figure 3. Infrared Spectra of Pure Oxirane Derivatives of Long-Chain 9-Mono-unsaturated Acids, Esters, and Alcohols

maxima, with consequent broadening and decrease of over-all intensity of the observed band.

Differences between spectra of solids and solutions are usually minor, as compared with those shown here, and the more marked differences are usually attributable to differences in degree of association through polar groups. The effect observed in this work, however, emphasizes the pitfalls that may be encountered in attempting to deduce molecular structure from spectra obtained on compounds in a given physical state on the basis of reference spectra obtained on them in a different state.

The authors have evidence that the spectra of some other solid oxygenated derivatives of the long-chain fatty acids, esters, and alcohols may depend on physical state. Additional oxygenated types are being investigated.

Spectra of Liquid Oxirane Compounds. The marked differences between spectra of the solid oxirane compounds in solution and in the solid state suggested a similar comparison between spectra of liquid compounds in the liquid and the solution state. Such a comparison was made for 1,2-epoxydecane, propylene oxide, and *cis*-methyl-9,10-epoxystearate (from methyl oleate). Except for a few slight shifts in the position of absorption maxima, and some changes in width of bands, the spectra of solutions closely resembled those shown in Figures 1, 2, and 3 for these compounds in the liquid state.

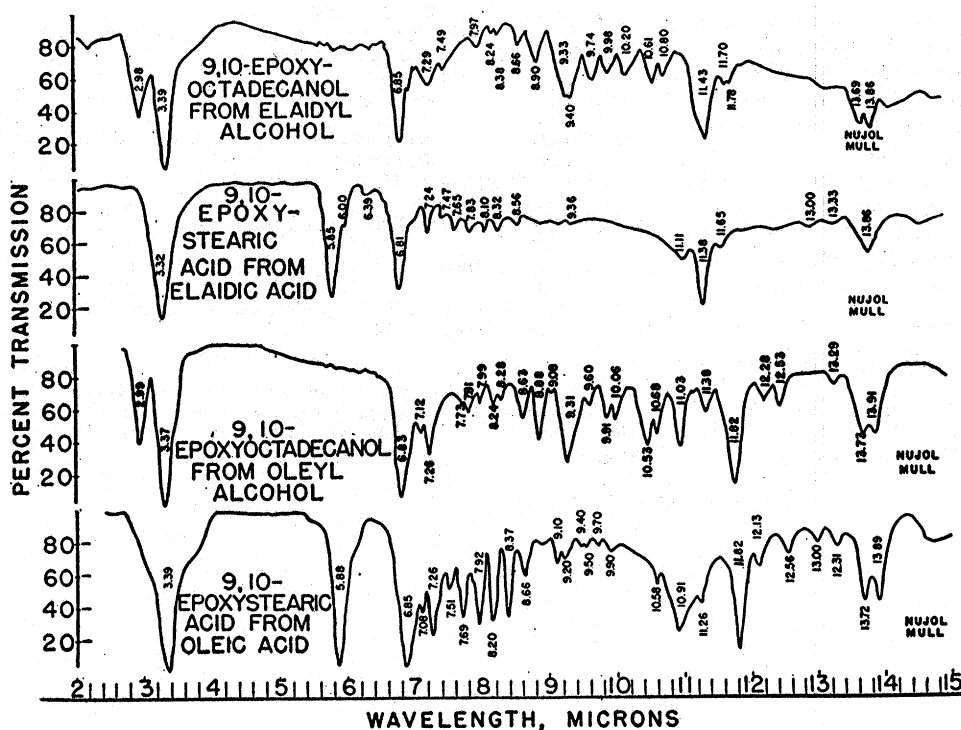


Figure 4. Infrared Spectra of Pure Oxirane Derivatives of Long-Chain 9-Mono-unsaturated Acids and Alcohols in the Solid State

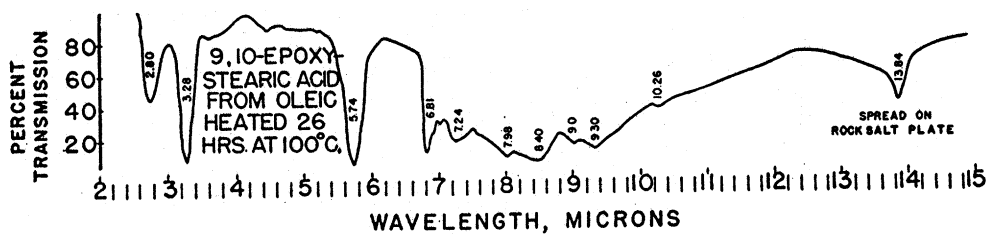


Figure 5. Infrared Spectrum of Thermally Polymerized *cis*-9,10-Epoxy stearic Acid

Comparison of Spectra of Stearic Acid and *n*-Octadecanol in the Solid State and in Solution. Again because of the marked effect of physical state on the spectra of the solid epoxy acids and alcohols, the spectra of stearic acid and *n*-octadecanol, previously reported as spectra of solutions (7), were redetermined in the solid state. In both, the 13.9-micron band became a doublet, and a few very weak new bands appeared in the 8-micron region in the spectrum of stearic acid and in the 10-micron region in the spectrum of *n*-octadecanol. The 9.5-micron O—H bending band in the spectrum of *n*-octadecanol became sharper, and the 2.7-micron O—H stretching band was

shifted to about 3 microns and intensified. In general, however, the over-all effect was less pronounced than that described above for the solid epoxy compounds.

Effect of Heat on Spectrum of 9,10-Epoxy stearic Acid. Thermal polymerization of the 9,10-epoxy stearic acids causes the disappearance of oxirane and carboxyl groups and the formation of secondary hydroxyl groups (8). The effect of such treatment on the spectrum is seen by comparing the spectrum of *cis*-9,10-epoxy stearic acid (Figure 4) with that of a sample which had been heated for 26 hours at 100° (Figure 5). The strong, sharp oxirane ring band near 11.8 microns and the band presumably due to carboxylic O—H bending near 10.9 microns have disappeared. A new band at 2.8 microns shows the formation of alcoholic hydroxyl groups, and the greatly increased absorption in the 8-micron region results from an increase in ester linkages. The sharp band structure characteristic of the crystal state has disappeared, and the CH₂ wagging absorption near 13.8 microns appears as a single band rather than as the doublet observed in the spectrum of the solid.

Other Epoxy Compounds. Figure 6 shows spectra of some

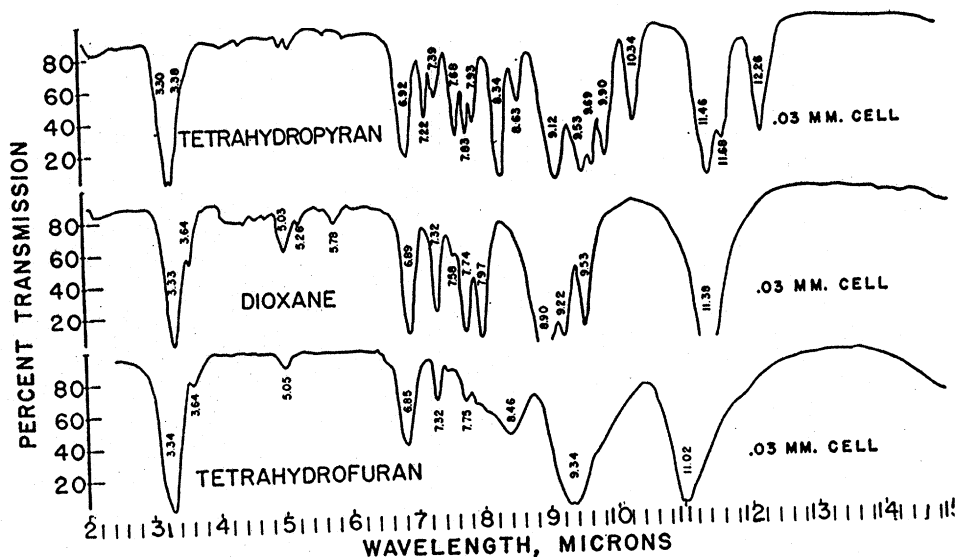


Figure 6. Infrared Spectra of Epoxy Compounds Containing 5- and 6-Membered Rings

epoxy compounds that contain 5- and 6-membered rings. In addition to strong ether absorption in the 9-micron region, these compounds show strong bands in the 11- to 12-micron region. Although additional reference spectra will be required before generalizing, the common band near 11.4 microns in the spectra of tetrahydropyran and dioxane is probably characteristic of the 6-membered heterocyclic oxygen ring in these compounds. Similarly, the 11-micron band in the tetrahydrofuran spectrum is probably characteristic of the 5-membered heterocyclic oxygen ring. The spectra of other compounds that contain similar rings confirm this assumption, but the purity of these additional compounds was not sufficiently certain to justify presentation of their spectra here.

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